

Advancements in Treatment of High-Salinity Wastewater: A Critical Review

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Abstract

Human life and the aquatic environment are negatively affected by the uncontrolled rapid discharge of high-salinity wastewater. There are many treatment processes, including physicochemical (membrane-based) and biological processes; however, owing to the high salinity rate in water effluents, there is a negative impact on the performance of these conventional treatment methods. Therefore, a hybrid treatment system specifically designed for high-salinity wastewater treatment was used. In the hybrid method, the membrane bioreactor (MBR) process is considered an effective treatment process in saline environments. The performance of membrane bioreactors (MBR) at different salinity levels was determined. Capacitive deionization (CDI) is an emerging treatment technology for high-salinity wastewater. Capacitive deionization (CDI) technology has proven to be a powerful process that is highly efficient compared to other treatment methods. The basic operation, adsorption-desorption of the electrode, different cell architectures, and parameters of various electrodes for capacitive deionization (CDI) are discussed. In addition, CDI emerging electrodes such as carbon nanotubes (CNTs) and graphene that eliminate the need for regeneration of saturated electrodes and comparison of capacitive deionization (CDI) with reverse osmosis (RO) is also a part of this review article.

Keywords: saline wastewater, membrane bioreactors, carbon nanotubes, reverse osmosis

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1. Introduction

The significant increase in the generation of wastewater is due to rapid population growth as well as industrialization [1]. It was found recently that the production of wastewater by different industries and agriculture sectors that has significantly high levels of salt [2]. When the wastewater contains a high concentration (0.5 to 3.4%) of organic pollutants and inorganic salts (such as NaCl and Na₂SO₄) then is referred to as "High-saline wastewater" [3]. The concentration of salinity is represented in the form of total dissolved solids (TDS), as well as in percentage (%), which expresses the total dissolved salt content. For example, it has been reported that in saline wastewater the salt content can vary from 0.2% to 15% depending upon the source from where it discharges. In addition to total dissolved solids (TDS) and percentage (%), salinity is also measured using electrical conductivity (EC) [4].

Different industries including aquaculture, pharmaceutical and textile industries are the main sources of saline-wastewater. These industries discharge a significant amount of saline-wastewater that contains organic and inorganic salt matters [5]. About 5 % of globally high saline effluents is originate from waste-water treatment plants [6]. Uncontrolled discharge of saline-effluents into water bodies causes serious impact on human life as well as on aquatic

environment [7]. It kills microbes and disrupts the mineral soil balance, which is essential for agricultural crops and the growth of several plants [8]. Therefore, it is necessary to treat saline wastewater before it is released into the environment to avoid pollution [8].

Many treatment methodologies have been used to treat saline effluents released from different sources. These treatment technologies are mainly based on physical, chemical and biological processes. Physicochemical treatments, such as membrane techniques, are commonly used to treat salinity from wastewater; however, this treatment consumes a lot of energy, takes a long time to start, is costly, and shows low efficiency at medium to high concentrations. [9]. Therefore, biological methods are more appropriate because they are economical, require fewer chemicals for operation, and produce fewer by-products. Despite their advantages, biological methods are inhibited in high-salinity wastewater because a high level of salt disrupts the metabolic function of the non-halophilic bacteria that are used in this method [6].

To overcome these treatment problems, this review explores several hybrid technologies including membrane bioreactors (MBR), capacitive deionization (CDI), and membrane capacitive deionization (MCDI) which are effective for the treatment of high salinity wastewater. The

latest desalination method in the 21st century is capacitive deionization (CDI), the main focus of this review is to explore the feasibility of CDI and emerging CDI electrode materials to encourage further research. In addition, the areas for improvement needed in this technology are also discussed.

2. Sources and impact of saline wastewater

In developing countries, the salinity of wastewater has increased dramatically. Many different sources of saline wastewater, along with their environmental effects, have been reported, which have been discussed below [10].

2.1. Genesis of saline wastewater

The salinity composition and concentration of the wastewater were determined using the source [11]. Saline wastewater is released into the environment from a variety of sources, including the direct use of seawater, agricultural runoff, and food processing and aquaculture industries, which negatively impacts treatment performance [12]. Owing to the limited availability of water resources globally, it is a more feasible option to use seawater directly for different purposes (such as toilets and road flushing) that are important to human life [13]. The drainage of seawater into sewers, which releases high-level saline wastewater, affects the degradation process of wastewater treatment plants [9]. When an area with saline alkali soil experiences excessive irrigation and rainfall, it changes and becomes a source of salinization [11]. Globally, approximately 20% of the agricultural land is threatened by salinity [14]. Agricultural drainage from saline farmlands produces saline wastewater, which contains high amounts of salt, fertilizer, and harmful pesticides and herbicides [15]. The absorption of these inorganic salts and contaminants in the soil causes land degradation, water quality deterioration, and serious agricultural development problems [16].

In addition, various industries, including fish processing, textiles, and tanneries, release high levels of salt during processing that pollute freshwater and groundwater. In recent times, aquaculture and fish-processing industries have grown tremendously worldwide, and they discharge wastewater containing high concentrations of salt, oil, antibiotics, and other contaminants [11]. In the fish processing industry, sodium chloride (NaCl) is frequently used to increase the efficiency of the cleaning process, which discharges 95% of non-reusable pollutants and becomes a source of eutrophication [17]. Another source of saline wastewater is the olive oil industry, which discharges approximately 0.5–2% of their salt into the environment. Their discharge contains phenolic compounds, which makes it difficult to treat wastewater [18]. The available literature review indicates that waste effluents released from pharmaceutical industries contain antibiotics, nitrogen, and inorganic salts ranging from 1000 to 30000 mg/L, which is a significant concern for both aquatic and human life [19].

2.2. Environmental impacts of saline wastewater

Salinity has a number of effects on ecosystems, including crop restrictions, deterioration of drinking water quality, and soil infertility. Approximately 7%–20% of the world's land and agricultural soil surfaces are affected by

salinity [19]. One of the biggest threats to agricultural land is soil salinization, which not only makes the soil infertile, but also affects its productivity and disturbs its osmotic balance [20]. It has been reported that the TDS level of groundwater affected by salinity ranges from 1500 to 3000 mg/L, which is a clear indication of soil salinization [21]. Furthermore, untreated saline wastewater also affects the quality of drinking water. Drinking water is affected by the surface runoff of saline wastewater that falls into freshwater streams and increases the salt and sulfate concentrations [22]. Salinity increases flooding and deteriorates infrastructure because the salt in wastewater is absorbed by the soil, preventing water from permeating the ground and weakening the structure [23]. Saline effluents discharged into water bodies also affect a variety of flora and fauna by disrupting their morphological features. Salt-sensitive plants are also affected at low salinity concentrations, which causes drastic effects on their growth [7]. The presence of salt in wastewater causes flocculation, which prevents light from entering water and disrupts the aquatic food chain [19]. Salinity also has a negative impact on various treatment methods, which has been thoroughly discussed in the sections below.

3. Conventional Treatment technologies for High Salinity wastewater

Various conventional treatment systems have been used to treat highly saline wastewaters (Fig.1). Saline wastewater treatment methods have gained popularity in recent decades because of their negative impact on treatment units. In this context, the performance of various physicochemical, and biological treatment techniques that have been reported for treatment of highly saline wastewater containing organic and inorganic impurities is discussed [24]

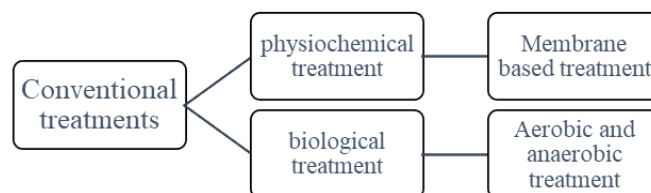


Fig. 1. Conventional treatment methodologies

3.1. Membrane-based processes: A Physiochemical treatment process

Physiochemical treatment methods are widely used for saline wastewater treatment. Adsorption, photo-catalysis, the Fenton process, coagulation-flocculation, and electrolysis are some of the most frequent physiochemical treatment processes [6]. All of these processes are very effective in wastewater treatment, but membrane-based processes have gained interest, especially in salinity treatment, because of their efficient capacities for pollutant removal, excellent permeate ability, easy handling, and recovery of resources [4]. A membrane-based process involves passing the effluent through a semi-permeable membrane that retains and permeates molecules based on their size and charge interactions [25]. In filtration, different conventional membrane modules are used, including flat sheets, spiral

wraps, and hollow fibers. To improve the performance and increase the filter efficiency, many innovative filter materials and pore structures have been developed, such as polysulfone, polyamide, cellulose, nylon, and polyethersulfone [26]. Some of these membrane techniques that are suitable for saline wastewater treatment are discussed here.

3.1.1. Reverse Osmosis

Reverse osmosis (RO) is a membrane-based pressure-driven process that removes monovalent and polyvalent pollutants, salts, and metals from water by applying hydrostatic pressure to a semipermeable membrane [27]. Pei et al. used a reverse osmosis membrane fabricated with polyamidoamine and trimesoyl chloride for high-salinity wastewater treatment that was discharged from the oil industry. Approximately 70% of the water was recovered, as 89.5% of the NaCl and 99% of the oil rejections were obtained [28]. However, the removal efficiency of reverse osmosis (RO) is affected by the salinity concentration in the wastewater, and when there is a high salt content in the feed water, the efficiency decreases. It was reported that when the salinity of wastewater discharged from the petrochemical industry increased from 0% to 35%, the efficiency of the RO process decreased by 4.5%. Another disadvantage of this process is that it is expensive and requires a large amount of energy to treat high saline concentrations [29-30].

3.1.2. Forward Osmosis

Forward osmosis (FO) is a process in which saline wastewater of varying concentrations passes through a membrane, and the solvent moves from a lower to a higher solute concentration. In this treatment, an osmotic membrane process, which uses less energy during separation, is applied. RO and FO differ primarily from one another because forward osmosis requires less pressure, generates high-quality water, has fewer membrane fouling issues, and requires less energy [31]. It has been reported that in saline wastewater treatment, emerging forward osmosis recovered approximately 50% of water and removed 90% to 97.7% of organic pollutants [32]. Forward osmosis is less expensive than reverse osmosis but still faces some major drawbacks, such as the required optimal operation parameters and membrane materials for enhancing the recovery rate of water flux [31-33].

3.1.3. Membrane distillation

Membrane distillation (MD) is an evaporative method that follows the vapor-liquid equilibrium principle, in which volatile molecules are separated through a membrane. This is a captivating membrane method because a trans-membrane with low pressure is used in this treatment [34]. Membrane distillation (MD) is the most widely used membrane-based technique for high-salinity environments. In MD, a water recovery rate of approximately 85% has been reported with the complete removal of inorganic pollutants [35]. The major disadvantage of this membrane technique is membrane fouling, which occurs because of the presence of proteins and polysaccharides in the saline wastewater. To reduce membrane fouling, it is suggested that pretreatment be

used to remove these organic compounds [27-36]. Another major drawback of the MD technique is that all the aforementioned membrane processes have low specific energy consumption (SEC), but MD has a high SEC and requires three times more energy for optimal vaporization [31-35]. Fig 2. Shows the specific energy consumptions of different membrane processes.

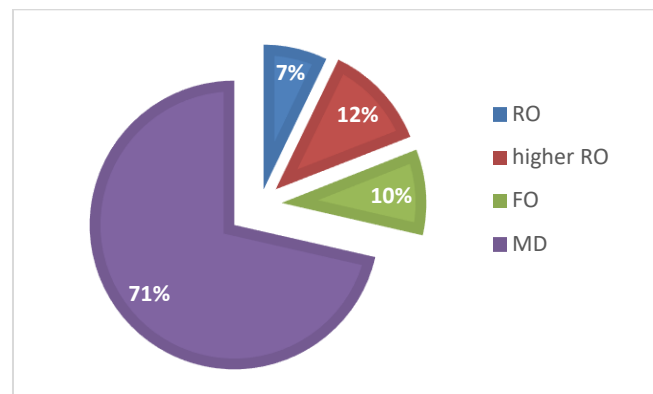


Fig. 1. Specific energy consumption of different membrane processes [31]

Despite their advantages, most membrane processes have a negative impact on high-salinity environments and alter the phase of pollutants. In Addition, high operational cost, produces secondary pollutants as a by-product and pre-treatment is required for removal of salt from wastewater [6-37].

3.2. Biological treatment processes

Biological methods are alternative treatments for saline wastewater discharge from different industrial sources. This treatment removes pollutants from waste products through the metabolism of microorganisms [38]. Compared with physiochemical treatment, aerobic and anaerobic biological treatment are more appropriate methods for salinity treatment because this method is more environment-friendly, highly effective, and stable [31]. In the literature, it was observed that in the biological method, activated sludge is effectively capable of treating salinity with a TDS of 4000 mg/L. However, if the salinity has a TDS above 4000 mg/L, its efficiency decreases. Therefore, to overcome this issue, bio-augmented systems are used in which halophilic microorganisms and biofilms are utilized to improve the efficiency of activated sludge at high salinities [39]. In recent years, research has been conducted on the configuration of biological methods, such as moving bed biofilm reactors and fed-batch reactors. These reactor systems perform very efficiently under low to medium salinity concentrations, and under high salinity, microbial deaths and misbalancing of osmotic pressure occur, lowering system efficiency [31-40].

4. Hybrid Treatment Technologies for High Saline Wastewater

Hybrid treatment methods have been extensively employed for saline wastewater treatment owing to their low sensitivity and high salinity. Over recent year, the application of hybrid methods, which combine two or more methods such as various physicochemical and biological processes, has

been emerging rapidly to protect the environment from saline effluents [41-42].

4.1. Membrane Bioreactor (MBR)

Membrane bioreactors (MBR) are one of the gold-standard hybrid methods for treating salinity [43]. In a common membrane bioreactor (MBR), the bioreactor is packed with activated sludge and fitted with a membrane filtration system. It has two different configurations, submerged MBR (SMBR) and side-stream MBR architecture, which were used to overcome the energy consumption of the MBR. In the Submerged MBR, the membrane is placed outside the bioreactor, while in the side-stream MBR, the membrane is placed inside the bioreactor that enables the treatment of saline water [44]. The membrane bioreactor (MBR) process is very popular worldwide owing to its number of benefits, including less sludge production, recovery of high-quality water, elimination of the sludge settling problem, complete removal of organic contaminants, and a higher concentration of biomass. The high biomass concentrations and high sludge retention time (SRT) make membrane bioreactor an ideal system for the treatment of industrial saline effluents [45]. Jemi et al. evaluated the efficiency of membrane bioreactors and conventional activated sludge (CAS) under high salinity wastewater and found that membrane bioreactors (MBR) completely eliminates the contaminant and is more efficient than conventional activated sludge. The chemical oxygen demand (COD) removal in MBR is 98.6% which is far better than CAS [46].

4.1.1. Effects of salinity on MBR performances

Membrane bioreactor (MBR) processes under salinity ranging from 0% to 10% are effective, and the chemical oxygen demand removal rate varies from 55% to 99%, indicating that non-halophilic microorganisms are resistant to high salinity. On the other hand, the total nitrogen removal rate varied between 17%-99%. This broad range removal is only obtained due to autotrophic microorganisms [8-47]. The integration of membrane bioreactors with other bioreactors that provide better biodegradation efficiencies improves the removal efficiency in high-salinity environments [48]. After this hybrid MBR treatment, approximately 93% of the chemical oxygen demand (COD) was removed, and a nitrogen removal rate of nearly 100% was reported. Pretreatment has proven to be a successful methodology for improving the efficiency of conventional membrane bioreactors for the treatment of saline wastewater. Moreover, Halophilic microorganisms, which are salt tolerant microbes used hybrid MBR systems for hyper saline wastewaters treatment without any pre-treatment [8]. Table 1 shows efficiency of different MBR plants treating saline wastewater.

Table 1. MBR plants treating saline wastewater

Bioreactors	Salinity (g NaCl L ⁻¹)	Removal of pollutants (COD)
MBR	2-5	80%
MBBR-Imbr	0-15	81%
Ion exchange + UASB + MBR	23	95%
BCOR-MBR	0-30	90%-96%

4.1.2. Effect of salinity on membrane fouling

An MBR is an efficient hybrid treatment; however, its major drawback is membrane fouling. There are a variety of membrane fouling mechanisms that have been discussed in the literature, but in saline wastewater treatment, Membrane fouling is increasing by Accumulation of hydrophobic extracellular polymeric substances (ESP) that are generated from activated sludge and also by soluble microbial product (SMP) that blocks inner pores of membrane [49-50]. In MBR, the amount of EPS and SMP production depends on the microorganism, where non-halophilic microbes generate high ESP and SMP, whereas halophilic microbes generate less ESP and SPM [51]. ESP and SMP are organic pollutants that only degraded by microbes [8]. In an MBR system, anti-membrane fouling is required for efficient degradation of saline wastewater. The microorganism community is an essential parameter for obtaining anti-membrane fouling in MBR. When an MBR system having non-halophilic microbes inoculate the halophilic microbes that favors degradation of high saline environments and also eliminate the production of EPS and SMP [8].

5. Capacitive Deionization (CDI) an Advance Saline wastewater treatment technique

Capacitive deionization (CDI) is an emerging 21st century technique that is a better alternative to other existing desalination techniques. CDI has a variety of different benefits, such as the fact that this technique, based on the electro-adsorption principle, consumes less energy and does not require any external pressure; it can operate in distant places where access to electricity poses a serious challenge and has very low water rejection and high water recovery [52]. The capacitive deionization system has two porous electrodes that are generally carbon electrodes and are separated by porous dielectric substances with a potential difference of 1–1.4 V [53-54]. Saline wastewater is passed through these porous electrodes, which have a positive and negative charge on them. Saline wastewater starts moving into the electric double layer, and unwanted ions present in the waste effluents are eliminated and held on the porous electrode surface. These inorganic ions clud to the electrode until the brine water was cleaned and the CDI cell was empty. After this step, ions are released by reversing the polarity

during the de-sorption phase, during which energy is recovered. A CDI system unit completes thousands of adsorption–desorption cycles [55].

6. Cell architectures used for CDI

In recent years, there has been much interest in the design of CDI cells. Two types of electrodes are used for CDI cell architecture: such as static electrodes (flow between and MCDI) and second is flow electrode architecture in which carbon slurry (FCDI) continuously moves to desalinate feed water [56].

6.1. Flow between electrode architecture

In 1960, Blair and Murphy proposed flow by electrode cell architecture. It comprises two permeable carbon electrodes split by a spacer, at which high-salinity wastewater flows adjacent to the applied potential. This cell architecture is most frequently and widely used to calculate the maximum salt adsorption capacity (mSAC) and the efficiency of porous materials used for electrodes [57].

6.2. Membrane CDI (MCDI)

The major modification of the capacitive deionization cell architecture is the addition of an ion-exchange membrane at the front of the carbon electrodes, which is called membrane CDI (MCDI). The MCDI was introduced by Andelman presented the MCDI idea in 2004 and is called the charge barrier flow capacitor [58]. In 2006, Lee demonstrated the MCDI system, which uses anion exchange (AEX) and cation exchange (CEX) membranes on top of the anode and cathode, respectively, to desalinate wastewater from thermal power plants. They stated that the salt elimination rate was 19% more efficient than conventional CDI, and the energy recovery rate for MCDI was 83% higher than that for CDI. MCDI has two significant advantages: first, the ion-exchange membrane prevents co-ions from leaving the surface of the electrode, increasing the salt adsorption capacity (SAC); and second, during the desorption step, it completely flushes the counter-ions, regenerating the porous electrode for the next adsorption phase [59].

6.3. Carbon flow electrode CDI (FCDI)

In this type of architecture, the slurry, made up of carbon, continuously moves through the electrode chambers with two opposing charges. The cations move towards the cathode, whereas the anions move towards the anode and are electro adsorbed [52]. The primary benefit of the FCDI architecture is the continuous flow of uncharged carbon slurry around the compartment, where adsorption and desorption of ions occur in a different compartment downstream. Jeon claimed that its desalination efficiency was 95% higher than that of the conventional CDI system units [60].

7. Parameters of CDI electrodes

Over the past ten years, capacitive deionization has increased tremendously. As a result, it is necessary to standardize CDI cell performance. The porosity, pore size,

volume, and specific surface area of active carbon materials are some of the factors that influence electrode efficiency [61].

7.1. Maximum Salt Adsorption Capacity (mSAC)

The most important parameter in CDI for defining a unit's performance is its salt adsorption capacity (SAC). It was first introduced in the CDI system during the charging-discharging phase. The maximum salt adsorption capacity was calculated by dividing the total rate of salt removal by the total rate of adsorbent weight, and expressing the result in (mg/g) of the electrode. The maximum SAC of the electrode, also known as the equilibrium salt adsorption capacity (eq SAC), was calculated. The cell voltage and salt content of the feed water must remain constant throughout the adsorption (charging) phase to obtain eqSAC [62-63]. The maximum salt adsorption capacity (mSAC) was calculated by multiplying the total change in the wastewater concentration over a period of time by the flow rate, which is the overall net volume of water passed to attain equilibrium. In a CDI system unit, it is the only property of the electrode that remains unaffected when all the other operating parameters are constant and is a widely used parameter for evaluating the performance of porous electrode materials [52]. The Fig. 3 shows the salt adsorption capacities of the different electrode materials.

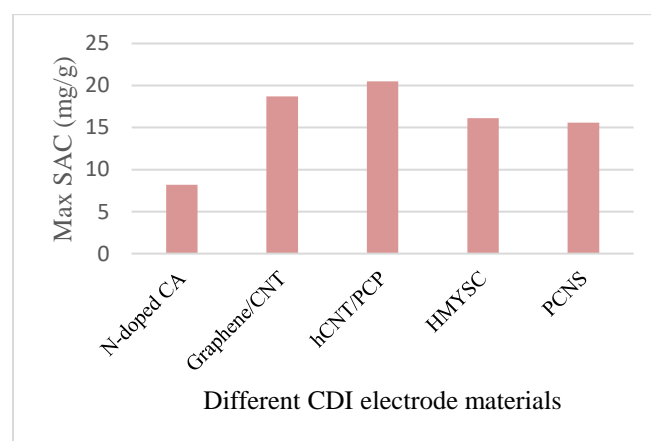


Fig. 3. Salt adsorption capacity of different electrode materials

7.2. Charge efficiency on electrode

Charge efficiency is defined as the ratio of adsorbed salt to charge. In 2009, Avraham coined the term "charge efficiency," and Zhao used the symbol Λ to describe it. The voltage of the cell and feed water salt content were determined by the charge efficiency. The charge efficiency (Λ) generally increased with increasing charge voltage and decreased with decreasing salt concentration and is an important parameter for analyzing CDI cell performance. In this metric, charge efficiency accounts for the energy requirement, with a higher charge efficiency and lower energy consumption [64]. The energy consumption in membrane CDI was compared with the energy consumption of a conventional CDI system at a constant voltage and current. This indicates that membrane CDI (MCDI) has greater charge efficiency and hence consumes less energy than conventional CDI because it prevents the inclusion of co-ions on porous carbon electrodes that occurs in conventional CDI [58].

7.3. Porosity on the electrode

The porosity of the electrode is one of the most important parameters in the CDI technique because it affects the adsorption and electro-sorption performance. The capacitance of the CDI electrodes was determined by the number of accessible pores and their size. IUPAC divides pores into three categories: macro-pores (> 50 nm), meso-pores (2 and 50 nm), and micro-pores (less than 2 nm) [65]. The traditional electrical double layer (EDL) theory proposes that the majority of electro-sorption and adsorption occurs in meso-pores; however, in one study, it was found that electro-sorption also occurs in the micro-pore electrode. As a result, both micro-pores and meso-pores are required in carbon materials to enhance capacitance and ion adsorption efficiency [66]. One study used three meso-porous, porous electrodes with 3D-cubic, 3D-bicontinuous, and 2D-hexagonal pore openings. According to this study, 2D hexagonal electrode structure allow monovalent ions to adsorb in pore walls. The 3D-cubic electrode space allows both monovalent and trivalent ions. 3D-bicontinuous pore opening electrode, not show any electro-sorption ability. The reason behind this no adsorption is due to pore structure of bi-continuous. The performance comparison of some electrode materials with different specific surface areas is presented in the fig. 4 [59].

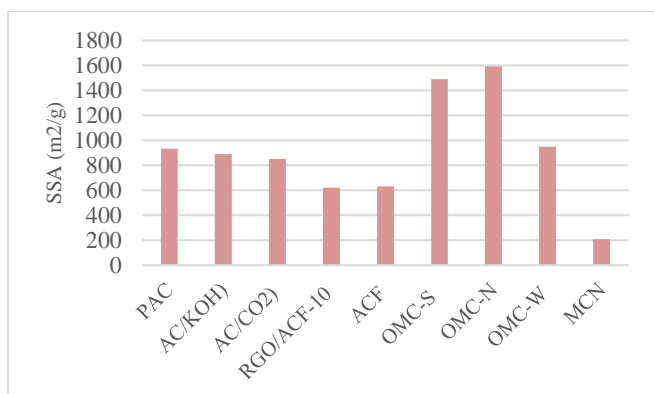


Fig. 4. Different electrodes with different specific surface area (SSA)

8. Emerging CDI electrode materials

Despite the fact that CDI has several advantages over other methods, the complete access to feasible novel electrode materials with high electro-adsorption and high salt-adsorption capacity (SAC) is a limitation. Large surface areas, high porosity, electrical conductivity, high electrochemical stability, bio-inertness, rapid adsorption-desorption occurs, and less costly, all desirable qualities in CDI electrode materials [67].

8.1. Carbon Nanotubes (CNTs)

Carbon compounds with one-dimensional (1D) tubular structures, known as carbon nanotubes (CNTs), are fabricated by rolling graphene layers. Carbon nanotubes have an advantage over other porous carbon materials because they carry a higher electrical intensity through tubes without electronic scattering [62]. Yan et al. (2012) used in situ polymerization to create SWCNT and polyaniline (PANI)

composites and observed a significant increase in the mesopore volume, which enhanced the removal efficiency by up to 12% above SWCNTs [68]. Wang et al. synthesized sponge electrodes of carbon nanotubes using chemical vapor deposition (CVD), in which 1, 2 dichlorobenzene was used as the carbon precursor and ferrocene was used as the catalyst. The CDI cell architecture was fabricated using CNT sponge electrodes without any binding agent, and it was claimed that their desalination capacity was 40 mg/g of electrodes, which was relatively high at that time [69].

8.2. Graphene based electrodes

In 2004, the discovery of graphene attracted considerable attention. Several graphene-based electrodes have been developed for CDI applications in recent years. Graphene is a carbon-based substance with a large surface area, excellent electrical conductivity, high antibacterial properties, chemical inertness, low density, and configurable functionalization, making it a potential host for composite electrode materials and water purification applications [70]. Graphene nanoflakes were utilized as CDI electrode materials, demonstrating that their electro-adsorption capability was higher than that of an activated carbon electrode. CDI electrodes were fabricated from three-dimensional macro-porous graphene architectures (3DMGA) [71]. These three-dimensional macro-porous graphene electrodes showed better capacitance (58.4 F/g) than traditional graphene electrodes (35/3 F/g) and electro-sorption capacity (3.9 mg/g) than traditional 3D graphene (2.5 mg/g) and activated carbon (2.9 mg/g). Graphene-mesoporous carbon nanosphere-grafted (GN/MCS) electrodes showed a higher capacitance (211 F/g) than graphene (73 F/g) and mesoporous carbon (164 F/g). These electrodes are specially developed for supercapacitors and can be used as electrodes in CDI cells in future research [59].

9. CDI Energy Consumption Compared to Reverse Osmosis (RO)

The desalination methods currently in use include reverse osmosis (RO), electro dialysis, thermal evaporation, and capacitive deionization (CDI). The most prominent methods are RO and CDI, which are used in approximately 85% of desalination plants [72]. Reverse osmosis (RO) uses external pressure to eliminate water from the dissolved solids. However, capacitive deionization (CDI) separates ions to generate clean freshwater in the absence of an external pressure. The minimum energy required for the removal of ions in an RO plant is determined by the input-output relationship between the total dissolved salt concentration and the water recovery rate [73-74]. When the salinity concentration increased to 8 g/L, the energy consumption in the RO plant rises to 6.5 kWh/m³. However, when a potential difference is applied, CDI electro adsorbs ions from saline wastewater in traditional double-layer electrodes (EDL), and the regeneration process recovers the energy. Consequently, the total energy required was the difference between the adsorption and desorption steps. Because energy is retrieved during the de-sorption step, the system is more energy-efficient than other methodologies. For many reasons, the CDI process consumes less energy than reverse osmosis. For example, CDI operates at low voltages and currents with low-

pressure pumps, whereas RO uses a high external pressure to overcome membrane resistance. CDI used 0.1 kWh/m³ of energy to remove high-salinity wastewater with a TDS of 2000 mg/L. Thus, it was concluded that even with a moderate efficiency of 60-70%, CDI requires 60% less energy than RO does [52-75].

10. Conclusions

In this review, different methodologies have been analyzed for the treatment of high-salinity wastewater, such as membrane-based processes, biological processes, and their combinations. Among these treatment methods, capacitive deionization (CDI) has proven to be a powerful process that is highly efficient in removing salinity from wastewater. CDI consumes less energy, is more environmentally friendly, and is less expensive than membrane-based processes. Many efforts have been made to explore and discover various types of novel electrodes with high salt adsorption capacities and to improve the efficiency of existing carbon-based electrodes by using different cell architectures to obtain a better product yield. Thus, CDI technology paves the way for effluent removal technology and has become an alternative option for deionization/desalination in the future, where cost and energy savings are vital issues and sources of freshwater are scarce.

11. Conclusions and future perspectives

Capacitive deionization (CDI) is highly efficient for generating deionized water because it is aimed at separating salts from water effluents. However, research on CDI is ongoing, and there are areas that still need greater focus, such as high surface area, which is required for effective adsorption; however, some electrode materials with inherently high surface areas still show lower removal capacities. The selection of electrodes with the desired pore size distribution for a more efficient adsorption of ions is also a critical issue that needs to be resolved in upcoming CDI-related research. Carbon electrodes also store energy (such as in super capacitors) along with ions. However, this aspect of CDI technology has not been extensively investigated. A good understanding of this area would help in recovering this energy, which in turn would reduce the cost and energy requirements of a CDI system.

Reference

- [1] A. Majumder, A.K. Gupta, P.S. Ghosal, M. Varma. (2021). A review on hospital wastewater treatment: A special emphasis on occurrence and removal of pharmaceutically active compounds, resistant microorganisms, and SARS-CoV-2. *Journal of environmental chemical engineering*. 9(2): 104812.
- [2] G. Zhou, X. Wang, H. Zhao, W. Zhang, G. Liu, X. Zhang. (2020). Isolation of two salt-tolerant strains from activated sludge and its COD degradation characteristics from saline organic wastewater. *Scientific reports*. 10(1): 1-13.
- [3] M. Zhang, F. Han, H. Chen, J. Yao, Q. Li, Z. Li, W. Zhou. (2022). The effect of salinity on ammonium-assimilating biosystems in hypersaline wastewater treatment. *Science of The Total Environment*. 829: 154622.
- [4] N.N.R. Ahmad, W.L. Ang, C.P. Leo, A.W. Mohammad, N. Hilal. (2021). Current advances in membrane technologies for saline wastewater treatment: A comprehensive review. *Desalination*. 517: 115170.
- [5] M. Pounsamy, S. Somasundaram, S. Palanivel, R. Balasubramani, S.W. Chang, D.D. Nguyen, S. Ganesan. (2019). A novel protease-immobilized carbon catalyst for the effective fragmentation of proteins in high-TDS wastewater generated in tanneries: Spectral and electrochemical studies. *Environmental research*. 172: 408-419.
- [6] A. Srivastava, V.K. Parida, A. Majumder, B. Gupta, A.K. Gupta. (2021). Treatment of saline wastewater using physicochemical, biological, and hybrid processes: Insights into inhibition mechanisms, treatment efficiencies and performance enhancement. *Journal of environmental chemical engineering*. 9(4): 105775.
- [7] H.N.P. Vo, H.H. Ngo, W. Guo, S.W. Chang, D.D. Nguyen, Z. Chen, X.C. Wang, R. Chen, X. Zhang. (2020). Microalgae for saline wastewater treatment: a critical review. *Critical Reviews in Environmental Science and Technology*. 50(12): 1224-1265.
- [8] X. Tan, I. Acquah, H. Liu, W. Li, S. Tan. (2019). A critical review on saline wastewater treatment by membrane bioreactor (MBR) from a microbial perspective. *Chemosphere*. 220: 1150-1162.
- [9] Y. Zhao, X. Zhuang, S. Ahmad, S. Sung, S.-Q. Ni. (2020). Biotreatment of high-salinity wastewater: current methods and future directions. *World Journal of Microbiology and Biotechnology*. 36(3): 1-11.
- [10] J. Church, J.-H. Hwang, K.-T. Kim, R. McLean, Y.-K. Oh, B. Nam, J.C. Joo, W.H. Lee. (2017). Effect of salt type and concentration on the growth and lipid content of *Chlorella vulgaris* in synthetic saline wastewater for biofuel production. *Bioresource technology*. 243: 147-153.
- [11] Y. Liang, H. Zhu, G. Banuelos, B. Yan, Q. Zhou, X. Yu, X. Cheng. (2017). Constructed wetlands for saline wastewater treatment: A review. *Ecological Engineering*. 98: 275-285.
- [12] X.-T. Bui, B.-T. Dang, T.-T. Nguyen, V.-T. Nguyen, D.P. Tran, P.-T. Nguyen, M. Boller, K.-Y.A. Lin, S. Varjani, P.L. Show. (2021). Influence of organic loading rates on treatment performance of membrane bioreactor treating tannery wastewater. *Environmental Technology & Innovation*. 24: 101810.
- [13] N. Voutchkov. (2018). Energy use for membrane seawater desalination—current status and trends. *Desalination*. 431: 2-14.
- [14] F. Cassel, S. Sharma. (2018). Delocalization of salt solution in a semiarid farmland topsoil. *Water, Air, & Soil Pollution*. 229: 1-8.
- [15] B. Sun, L. Zhang, L. Yang, F. Zhang, D. Norse, Z. Zhu. (2012). Agricultural non-point source pollution in China: causes and mitigation measures. *Ambio*. 41: 370-379.
- [16] Y. Zhao, X. Zhuang, S. Ahmad, S. Sung, S.-Q. Ni. (2020). Biotreatment of high-salinity wastewater: current methods and future directions. *World*

- Journal of Microbiology and Biotechnology. 36: 1-11.
- [17] T.N.-D. Cao, X.-T. Bui, L.-T. Le, B.-T. Dang, D.P.-H. Tran, H.-T. Tran, T.-B. Nguyen, H. Mukhtar, S.-Y. Pan, S. Varjani. (2022). An overview of deploying membrane bioreactors in saline wastewater treatment from perspectives of microbial and treatment performance. *Bioresource technology*. 127831.
- [18] A.Y. Gebreyohannes, E. Curcio, T. Poerio, R. Mazzei, G. Di Profio, E. Drioli, L. Giorno. (2015). Treatment of olive mill wastewater by forward osmosis. *Separation and Purification Technology*. 147: 292-302.
- [19] D. Marathe, A. Singh, K. Raghunathan, P. Thawale, K. Kumari. (2021). Current available treatment technologies for saline wastewater and land-based treatment as an emerging environment-friendly technology: A review. *Water Environment Research*. 93(11): 2461-2504.
- [20] J. Huang, M.J. Prochazka, J. Triantafilis. (2016). Irrigation salinity hazard assessment and risk mapping in the lower Macintyre Valley, Australia. *Science of The Total Environment*. 551: 460-473.
- [21] M. El-Fadel, T. Deeb, I. Alameddine, R. Zurayk, J. Chaaban. (2018). Impact of groundwater salinity on agricultural productivity with climate change implications. *International Journal of Sustainable Development and Planning*. 13(3): 445-456.
- [22] M.S. Schuler, M. Canedo-Argüelles, W.D. Hintz, B. Dyack, S. Birk, R.A. Relyea. (2019). Regulations are needed to protect freshwater ecosystems from salinization. *Philosophical Transactions of the Royal Society B*. 374(1764): 20180019.
- [23] A. Singh. (2015). Soil salinization and waterlogging: A threat to environment and agricultural sustainability. *Ecological indicators*. 57: 128-130.
- [24] H. Mirbolooki, R. Amirzhad, A.R. Pendashteh. (2017). Treatment of high saline textile wastewater by activated sludge microorganisms. *Journal of applied research and technology*. 15(2): 167-172.
- [25] A. Rathore, A. Shirke. (2011). Recent developments in membrane-based separations in biotechnology processes. *Preparative Biochemistry and Biotechnology*. 41(4): 398-421.
- [26] H.A. Maddah, A.S. Alzhrani, M. Bassyouni, M. Abdel-Aziz, M. Zoromba, A.M. Almalki. (2018). Evaluation of various membrane filtration modules for the treatment of seawater. *Applied Water Science*. 8: 1-13.
- [27] R. Alam, S.U. Khan, M. Usman, M. Asif, I.H. Farooqi. (2022). A critical review on treatment of saline wastewater with emphasis on electrochemical based approaches. *Process Safety and Environmental Protection*. 158: 625-643.
- [28] B. Pei, J. Chen, P. Liu, T. He, X. Li, L. Zhang. (2018). Hyperbranched poly (amidoamine)/TMC reverse osmosis membrane for oily saline water treatment. *Environmental technology*.
- [29] T. Ahmad, C. Guria, A. Mandal. (2018). Synthesis, characterization and performance studies of mixed-matrix poly (vinyl chloride)-bentonite ultrafiltration membrane for the treatment of saline oily wastewater. *Process Safety and Environmental Protection*. 116: 703-717.
- [30] M.A. Hanif, R. Nadeem, M.N. Zafar, K. Akhtar, H.N. Bhatti. (2007). Kinetic studies for Ni (II) biosorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass. *Journal of Hazardous Materials*. 145(3): 501-505.
- [31] P. Sahu. (2021). A comprehensive review of saline effluent disposal and treatment: conventional practices, emerging technologies, and future potential. *Journal of Water Reuse and Desalination*. 11(1): 33-65.
- [32] E.O. Ezugbe, E. Kweinor Tetteh, S. Rathilal, D. Asante-Sackey, G. Amo-Duodu. (2021). Desalination of municipal wastewater using forward osmosis. *Membranes*. 11(2): 119.
- [33] D. Roy, M. Rahni, P. Pierre, V. Yargeau. (2016). Forward osmosis for the concentration and reuse of process saline wastewater. *Chemical Engineering Journal*. 287: 277-284.
- [34] H. Susanto. (2011). Towards practical implementations of membrane distillation. *Chemical Engineering and Processing: Process Intensification*. 50(2): 139-150.
- [35] A. Hanif, S. Ali, M.A. Hanif, U. Rashid, H.N. Bhatti, M. Asghar, A. Alsalmeh, D.A. Giannakoudakis. (2021). A novel combined treatment process of hybrid biosorbent-nanofiltration for effective Pb (II) removal from wastewater. *Water*. 13(23): 3316.
- [36] G. Naidu, S. Jeong, Y. Choi, S. Vigneswaran. (2017). Membrane distillation for wastewater reverse osmosis concentrate treatment with water reuse potential. *Journal of Membrane Science*. 524: 565-575.
- [37] M.A. Hanif, R. Nadeem, M.N. Zafar, H. Bhatti, R. Nawaz. (2008). Physico-chemical treatment of textile wastewater using natural coagulant cassia. *J. Chem. Soc. Pak*. 30(3): 385.
- [38] C. Narayanan, V. Narayan. (2019). Biological wastewater treatment and bioreactor design: a review. *Sustainable environment research*. 29(1): 1-17.
- [39] V. Alipour, F. Moein, L. Rezaei. (2017). Determining the salt tolerance threshold for biological treatment of salty wastewater. *Health Scope*. 6(1).
- [40] S. Abdelkader, F. Gross, D. Winter, J. Went, J. Koschikowski, S.U. Geissen, L. Bousselmi. (2019). Application of direct contact membrane distillation for saline dairy effluent treatment: performance and fouling analysis. *Environmental Science and Pollution Research*. 26: 18979-18992.
- [41] W. Song, Z. Li, Y. Ding, F. Liu, H. You, P. Qi, F. Wang, Y. Li, C. Jin. (2018). Performance of a novel hybrid membrane bioreactor for treating saline wastewater from mariculture: Assessment of pollutants removal and membrane filtration performance. *Chemical Engineering Journal*. 331: 695-703.
- [42] A. Ashfaq, R. Nadeem, S. Bibi, U. Rashid, M.A. Hanif, N. Jahan, Z. Ashfaq, Z. Ahmed, M. Adil, M.

- Naz. (2021). Efficient Adsorption of Lead Ions from Synthetic Wastewater Using Agrowaste-Based Mixed Biomass (Potato Peels and Banana Peels). *Water*. 13(23): 3344.
- [43] D. De Jager, M.S. Sheldon, W. Edwards. (2012). Membrane bioreactor application within the treatment of high-strength textile effluent. *Water Science and Technology*. 65(5): 907-914.
- [44] L. Goswami, R.V. Kumar, S.N. Borah, N.A. Manikandan, K. Pakshirajan, G. Pugazhenth. (2018). Membrane bioreactor and integrated membrane bioreactor systems for micropollutant removal from wastewater: a review. *Journal of water process engineering*. 26: 314-328.
- [45] M. Capodici, A. Cosenza, G. Di Bella, D. Di Trapani, G. Viviani, G. Mannina. (2020). High salinity wastewater treatment by membrane bioreactors. *Current Developments in Biotechnology and Bioengineering*. 177-204.
- [46] M. Jemli, F. Karray, F. Feki, S. Loukil, N. Mhiri, F. Aloui, S. Sayadi. (2015). Biological treatment of fish processing wastewater: a case study from Sfax City (Southeastern Tunisia). *Journal of Environmental Sciences*. 30: 102-112.
- [47] I. Javed, M.A. Hanif, U. Rashid, F. Nadeem, F.A. Alharthi, E.A. Kazerooni. (2022). Enhancing Functionalities in Nanocomposites for Effective Dye Removal from Wastewater: Isothermal, Kinetic and Thermodynamic Aspects. *Water*. 14(17): 2600.
- [48] A. Akhtar, M.A. Hanif, U. Rashid, I.A. Bhatti, F.A. Alharthi, E.A. Kazerooni. (2022). Advanced Treatment of Direct Dye Wastewater Using Novel Composites Produced from Hoshanar and Sunny Grey Waste. *Separations*. 9(12): 425.
- [49] G. Di Bella, D. Di Trapani, S. Judd. (2018). Fouling mechanism elucidation in membrane bioreactors by bespoke physical cleaning. *Separation and Purification Technology*. 199: 124-133.
- [50] Y. Chauhdary, M.A. Hanif, U. Rashid, I.A. Bhatti, H. Anwar, Y. Jamil, F.A. Alharthi, E.A. Kazerooni. (2022). Effective removal of reactive and direct dyes from colored wastewater using low-cost novel bentonite nanocomposites. *Water*. 14(22): 3604.
- [51] G. Qiu, Y.-P. Ting. (2014). Short-term fouling propensity and flux behavior in an osmotic membrane bioreactor for wastewater treatment. *Desalination*. 332(1): 91-99.
- [52] S.S. Gupta, M.R. Islam, T. Pradeep, Capacitive deionization (CDI): an alternative cost-efficient desalination technique. In *Advances in Water Purification Techniques*, Elsevier: 2019; pp 165-202.
- [53] J.E. Dykstra. Desalination with porous electrodes: Mechanisms of ion transport and adsorption. Wageningen University and Research, 2018.
- [54] I. Akbar, M.A. Hanif, U. Rashid, I.A. Bhatti, R.A. Khan, E.A. Kazerooni. (2022). Green Nanocomposite for the Adsorption of Toxic Dyes Removal from Colored Waters. *Coatings*. 12(12): 1955.
- [55] E.T. Sayed, A. Olabi, N. Shehata, M. Al Radi, O.M. Muhaisen, C. Rodriguez, M.A. Atieh, M.A. Abdelkareem. (2022). Application of bio-based electrodes in emerging capacitive deionization technology for desalination and wastewater treatment. *Ain Shams Engineering Journal*. 102030.
- [56] M.E. Suss, T.F. Baumann, W.L. Bourcier, C. Spadaccini, M. Stadermann, K. Rose, J.G. Santiago, Flow-through electrode capacitive desalination. In *Google Patents*: 2012.
- [57] Y. Zhao, X.-m. Hu, B.-h. Jiang, L. Li. (2014). Optimization of the operational parameters for desalination with response surface methodology during a capacitive deionization process. *Desalination*. 336: 64-71.
- [58] R. Zhao, P. Biesheuvel, A. Van der Wal. (2012). Energy consumption and constant current operation in membrane capacitive deionization. *Energy & Environmental Science*. 5(11): 9520-9527.
- [59] M.A. Ahmed, S. Tewari. (2018). Capacitive deionization: Processes, materials and state of the technology. *Journal of Electroanalytical Chemistry*. 813: 178-192.
- [60] S.-i. Jeon, H.-r. Park, J.-g. Yeo, S. Yang, C.H. Cho, M.H. Han, D.K. Kim. (2013). Desalination via a new membrane capacitive deionization process utilizing flow-electrodes. *Energy & Environmental Science*. 6(5): 1471-1475.
- [61] A.G. El-Deen, N.A. Barakat, H.Y. Kim. (2014). Graphene wrapped MnO₂-nanostructures as effective and stable electrode materials for capacitive deionization desalination technology. *Desalination*. 344: 289-298.
- [62] I.D. Costa, A.d.O. Wanderley Neto, H.F.O. da Silva, E.P. Moraes, E.T. Damascena Nóbrega, C. Sant'Anna, M. Eugenio, L.H.d.S. Gasparotto. (2017). Dual role of a ricinoleic acid derivative in the aqueous synthesis of silver nanoparticles. *Journal of Nanomaterials*. 2017.
- [63] M.I. Jilani, R. Nadeem, M.A. Hanif, T. Mahmood Ansari, A. Majeed. (2015). Utilization of immobilized distillation sludges for bioremoval of Pb (II) and Zn (II) from hazardous aqueous streams. *Desalination and Water Treatment*. 55(1): 163-172.
- [64] Z.-H. Huang, M. Wang, L. Wang, F. Kang. (2012). Relation between the charge efficiency of activated carbon fiber and its desalination performance. *Langmuir*. 28(11): 5079-5084.
- [65] S. Zhao, T. Yan, Z. Wang, J. Zhang, L. Shi, D. Zhang. (2017). Removal of NaCl from saltwater solutions using micro/mesoporous carbon sheets derived from watermelon peel via deionization capacitors. *RSC advances*. 7(8): 4297-4305.
- [66] Q. Imran, M. Hanif, M. Riaz, S. Noureen, T. Ansari, H. Bhatti. (2012). Coagulation/flocculation of tannery wastewater using immobilized chemical coagulants. *Journal of applied research and technology*. 10(2): 79-86.
- [67] A. Bazan-Wozniak, P. Nowicki, R. Pietrzak. (2018). Production of new activated bio-carbons by chemical activation of residue left after supercritical extraction of hops. *Environmental research*. 161: 456-463.
- [68] C. Yan, L. Zou, R. Short. (2012). Single-walled carbon nanotubes and polyaniline composites for

- capacitive deionization. *Desalination*. 290: 125-129.
- [69] X. Xu, M. Wang, Y. Liu, T. Lu, L. Pan. (2016). Metal–organic framework-engaged formation of a hierarchical hybrid with carbon nanotube inserted porous carbon polyhedra for highly efficient capacitive deionization. *Journal of Materials Chemistry A*. 4(15): 5467-5473.
- [70] S.-H. Lee, D. Kang, I.-K. Oh. (2017). Multilayered graphene-carbon nanotube-iron oxide three-dimensional heterostructure for flexible electromagnetic interference shielding film. *Carbon*. 111: 248-257.
- [71] M. Riaz, M. Hanif, S. Noureen, M. Khan, T. Ansari, H. Bhatti, Q. Imran. (2012). Coagulation/flocculation of tannery wastewater using immobilised natural coagulants. *Journal of Environmental Protection and Ecology*. 13(3A): 1948-1957.
- [72] T.M. Ansari, S. Shaheen, S. Manzoor, S. Naz, M.A. Hanif. (2020). Litchi chinensis peel biomass as green adsorbent for cadmium (Cd) ions removal from aqueous solutions. *Desalination and Water Treatment*. 173: 343-50.
- [73] R. Zhao, S. Porada, P. Biesheuvel, A. Van der Wal. (2013). Energy consumption in membrane capacitive deionization for different water recoveries and flow rates, and comparison with reverse osmosis. *Desalination*. 330: 35-41.
- [74] T.M. Ansari, M.A. Hanif, T. Rasool, M. Ali, R. Nadeem, M. Yaseen. (2016). Reclamation of wastewater containing Cu (II) using alginated *Mentha spicata* biomass. *Desalination and Water Treatment*. 57(23): 10700-10709.
- [75] A. Hanif, H.N. Bhatti, M.A. Hanif. (2015). Removal of zirconium from aqueous solution by *Ganoderma lucidum*: biosorption and bioremediation studies. *Desalination and Water Treatment*. 53(1): 195-205.